

**POLLUTANTS IN ROAD-DEPOSITED SEDIMENTS: CHARACTERISTICS,
MOBILITY, BIOAVAILABILITY AND REMEDIATION**

By

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**A Thesis submitted in fulfilment for the degree of
Doctor of Philosophy**



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CERTIFICATE OF AUTHORSHIP/ ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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DEDICATION THIS THESIS

TO MY HUSBAND AND MY DAUGHTER

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NOMENCLATURE

AET = apparent effects threshold

AhR = AhR aryl hydrocarbon receptor;

Ant = Anthracene

B[a]A = Benzo[a]anthracene

B[a]P = Benzo[a]pyrene

B[b]F = benzo[b]fluoranthene

B[ghi]P = benzo[g,h,i]perylene

B[k] = benzo[k]fluoranthene

BAET = benthic apparent effects threshold

BLS = Baseline soil

C_o = initial concentration of adsorbate (mg/L)

$Ca(OH)_2$ = Calcium hydroxide

Ca^{2+} = Calcium

CAFLUX = Chemically Activated Fluorescent Expression

C_e = equilibrium concentration of adsorbate (mg/L)

Chry = chrysene

C_o = inlet adsorbate concentration (mg/L)

C_s = the concentration on the external surface (mg/L)

C_t = concentration of adsorbate at time t (mg/L)

CYP1A1 = Cytochrome P450 1A1

DBA = dibenzo[a,h]anthracene

DOC = dissolved organic matter

DRE = dioxin response element

dw = dry weight

EC50 = estimated concentration needed to produce 50% of the maximal response

EROD = ethoxyresorufin O-deethylase

F = Fluorene

Fe^{3+} = Iron (III)

FeO = Zero-valent iron

Fl = Fluoranthene

FTIR = Fourier transform infrared spectroscopy

g/L = gram per litre

GAC = Granular activated carbon
 HA = Humic acid
 HACCP = Hazard Analysis and Critical Control Point
 HAH = halogenated aromatic hydrocarbons
 HCl = hydrochloric acid
 HCO_3^- = bicarbonate
 HFO = Hydrous ferric oxides
 HMW PAH = high molecular weight PAHs
 hr = hours
 HSDM = Homogeneous surface diffusion model
 ICZ = Iron-coated zeolite
 IND = indeno[1,2,3-cd]pyrene
 K^+ = Potassium
 k_1 = equilibrium rate constant of pseudo-first-order sorption (1/min)
 k_2 = equilibrium rate constant of pseudo-second-order (1/min)
 k_{AB} = kinetic constant, (L/mg.min)
 KNO_3 = Potassium nitrate
 KCl = Potassium chloride
 KF = Freundlich constants (mg/g)
 k_f = the external mass transfer coefficient (m/s)
 KH_2PO_4 = Monopotassium phosphate
 KL = Langmuir constant related to the energy of adsorption (L/mg)
 k_{Th} = Thomas rate constant (mL/min.mg)
 k_{YN} = rate velocity constant (1/min)
 LD50 = 50% lethal dose
 LMW PAH = low molecular weight PAHs
 LOEL = lowest observed effect level
 M = mass of dry adsorbent (g)
 m/h = meter per hour
 mg/L = milligram per litre
 MFO = mixed-function oxidase (or oxygenase) enzyme system
 min = minutes
 mL/min = millilitre per minute
 MW = Molecular weight

Na⁺ = Sodium
Na₂CO₃ = Sodium carbonate
Na₂SO₄ = Sodium sulphate
NaCl = sodium chloride
NaHCO₃ = sodium bicarbonate
NaNO₃ = sodium nitrate
NaOH = Sodium hydroxide
Nap = Naphthalene
NOEL = No observed effect level
NOM = Natural organic matter
P450 = Cytochrome P450
PAH = Polynuclear aromatic hydrocarbon
PCB = Polychlorinated biphenyl
PCDDs = Polychlorinated dibenzo-p-dioxins
Phe = Phenanthrene
Pyr = Pyrene
RDS = Road-deposited sediments
TCDD = 2,3,7,8-tetrachlorodibenzo-p-dioxin
TCDF = 2,3,7,8-tetrachlorodibenzofuran
TEF = Toxic equivalency factor
TCDD TEQ = Dioxin TCDD toxic equivalent quotient
TPAH = Total PAHs
WBS = Water baseline sediments
WUSD = Water Sensitive Urban Design
μ = Solution viscosity
XRD = X-ray powder diffraction
SEM = Scanning Electron Microscopy
EDS = Energy Dispersive Spectroscopy
TEQ = toxicity equivalent quotient

ABSTRACT

Rapid urbanization and associated ever-increasing motor-traffic density have led to escalating amounts of pollution along road-ways in the form of aerosols and road-deposited sediments (RDS) in many parts of the world. RDS contain many pollutants such as heavy metals, metalloids and polycyclic aromatic hydrocarbons (PAHs) which are derived from vehicle exhaust emissions, vehicle tyres, brakes, body frames, asphalt road surfaces, deicing salt, paint markers, and pesticides and herbicides added to the pavement. During heavy rain, these pollutants are washed into stormwater and transported into natural water bodies and this can cause potentially toxicity to aquatic organisms.

Road-deposited sediments (RDS), water baseline sediments (WBS) and baseline soil (BLS) samples from major urban roads in Kogarah Bay area, Sydney, were analyzed for several heavy metals/metalloids and polycyclic aromatic hydrocarbons (PAHs). RDS had elevated concentrations of Pb, Cd, Cu, Cr, Ni, Zn, Fe and PAHs. Both correlation and principal component analysis showed that Zn, Cu, Cr, and Sb in RDS probably originated from vehicle brakes and tyre wear while V originated mainly from road asphalt surface. The heavy metal concentrations were similar in WBS and BLS. Heavy metal fractionation data showed that potential mobility, an indication of their transportation by stormwater, decreased in the order Fe > Mn, Zn > Cu, Pb > Cr, Ni, V, Cd, Sb. Ecological risk as assessed by ISQG (Interim Sediment Quality Guidelines) and the method developed by Hakanson (1980) was low to medium in RDS and low in BLS and WBS. Of the heavy metals in RDS, Cu had the highest potential risk, whereas Zn had the lowest.

The concentrations of sixteen polycyclic aromatic hydrocarbons (PAH mg/kg) in the RDS, WBS and BLS ranged from 0.40 to 7.49 (mean 2.80), 1.65 to 4.00 (mean 2.91), and 0.46 to 1.41 (mean 0.84), respectively. PAH compounds had higher concentrations of high molecular weight compounds with three or more fused benzene rings indicating that high temperature combustion processes were their predominant sources. The proportions of high molecular weight PAHs were higher in BLS than in RDS, whereas the low molecular weight PAHs were higher in RDS. All PAH compounds were observed to be the lowest in WBS. All PAHs (except naphthalene) were significantly correlated in BLS suggesting a common PAH source. The ratios of individual diagnostic PAHs showed that the primary source of PAHs in WBS and BLS was pyrogenic (combustion of petroleum (vehicle exhaust), grass, and wood) and in

RDS was petrogenic (unburned or leaked fuel and oil, road asphalt) as well as pyrogenic. The potential toxicities of PAHs calculated using toxicity equivalent quotients were all low but higher for BLS than for WBS and RDS.

This study also investigated the toxic effects of RDS and BLS in a range of bioassays, using water elutriates of sediments from different sites to simulate contaminated receiving waters, and solvent extracts to represent the total contaminant levels. Chemical analyses showed that the total concentrations of metals and PAHs in the RDS were above sediment quality guidelines, and were higher in the finer size fractions. Metal and PAH levels in the BLS were well below guideline levels. To establish baseline toxicity data, acute *Artemia* nauplii tests were carried out with putatively identified compounds (heavy metals and PAHs identified from chemical analyses of similar sediments in Sydney), spiked into aqueous solutions and elutriates. In these tests, low molecular weight PAHs showed greater toxicity than high molecular weight PAHs. For both metals and PAHs, the toxicity was significantly higher when they were tested in clean water than in elutriates. However, neither RDS nor BLS elutriates caused any toxicity in a 24-hour acute test with *Artemia* nauplii. In the Microtox® assay, both RDS and BLS elutriates showed some toxicity; RDS samples were more toxic than the BLS, but there was no significant difference between size fractions. The response patterns in the Microtox® assays suggested effects from both heavy metals and organic compounds. The AhR CAFLUX bioassay, which is sensitive to dioxin-like compounds including PAHs, showed relatively lower activity in solvent extracts of RDS, with slightly higher activity in the finer fractions of the sediment. There was no detectable AhR CAFLUX activity in BLS. The p53 GeneBLAzer® assay, a measure of genotoxicity, showed no effect from any elutriates or solvent extracts of RDS or BLS. The results indicate that the RDS presents a greater hazard than the BLS, particularly in the finer size fractions. Accumulation of RDS in estuarine sediment may pose a risk to benthic organisms, especially those that feed on and in the sediments.

Iron coated zeolite (ICZ) was synthesized by adding natural zeolite in an iron nitrate solution under strongly basic conditions. ICZ was found to adsorb significantly larger amounts of heavy metals than zeolite, because of the specific adsorption of metals by the iron on the zeolite surface. The batch adsorption was satisfactorily explained using the Langmuir isotherm while the column adsorption data fitted reasonably well to the empirical Thomas model. Desorption of metals previously adsorbed on zeolite and ICZ columns by elution with

0.1 M HCl removed 62–90% and 58–85% of adsorbed metals in the first and second cycles of adsorption/desorption, respectively. Although the regeneration of ICZ reduced the adsorption capacity, partly because of the iron coatings being dissolved, the adsorption capacity of the regenerated ICZ was still higher than that of the original zeolite. In summary, the batch and fixed-column experimental results showed that ICZ is a potential adsorbent for removing heavy metals from aqueous solutions.

Industrial low-cost by-products such as blast furnace slag and fly ash were used to remove five heavy metals from water in batch and fixed bed column experiments. Increase of pH increased adsorption of all metals. Equilibrium adsorption of all metals was successfully modeled using Langmuir, Freundlich and Dubinin-Radushkevich models, with Freundlich model fitting the data the best. Langmuir adsorption maximum at pH 6.5 for fly ash ranged 3.4 - 5.1 mg/g with the adsorption capacity for the metals in the order, Pb > Cu > Cd, Zn, Cr. The corresponding values for furnace slag were 4.3 - 5.2 mg/g, and the order of adsorption capacities, Pb, Cu, Cd > Cr > Zn. The kinetics of adsorption fitted well to both the pseudo-first order and pseudo-second order models, but the fit was slightly better for the pseudo-second order model. The column experiments of furnace slags indicated that column process can be used for treating of waters containing a single heavy metal as well as for removal of mixtures of heavy metals. The effectiveness of the fixed bed columns with respect to heavy metal ions agreed well with the batch experiment. The mechanism of heavy metal removal may include ion exchange/adsorption and surface precipitation on the adsorbent.